Next nearest neighbor effects in triphylite and related phosphate minerals

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Abstract

Phosphate minerals of triphylite, ferrisicklerite and purpurite were investigated using Mössbauer spectroscopy. The crystal structures of these three minerals are alike to that of olivine except no atoms in the M1 site of purpurite structure. Mössbauer spectra of these minerals at 298K are composed of the multiple doublets with nearly equal isomer shifts but slightly different quadrupole splittings. These multiple doublets are assigned to Fe^{2+} or Fe^{3+} in the M2 sites, showing that the next nearest neighbor (NNN) effect exists in the Mössbauer spectra of these minerals.

Introduction

The known natural phosphate minerals exceed 250 in number. The details of crystal structures and chemistries of phosphate minerals have been gained largely from systematic crystal structure analyses. Moore (1984) presented a review on crystal chemistry of phosphate minerals. It is well known that ^{57}Fe Mössbauer effect can be used to study minerals and provide some useful information about crystal chemistry. However, only a few Mössbauer studies on phosphate minerals have been carried out.

Oxidation mechanism of vivianite was investigated by Takashima and Ohashi (1968), Tricker and Ash (1979), Vochten *et al.* (1979), Dormann and Poullen (1980), McCammon and Burns (1980) and Burns (1981). Kostiner (1972) presented the Mössbauer parameters of triplite, zwieselite, triploidite and wolfeite. Li *et al.* (1988b) explained the Mössbauer spectrum of triplite based on the effect of fluorine in the crystal structure of triplite. Cation distribution of some orthophosphates $(\text{Zn,Fe,Mg,Ni,Co})_3\text{PO}_4$ with farringtonite and olivine-related $(\text{Fe,Mn,Co,Mg})_3(\text{PO}_4)_2$ sarcopside structures were investigated by Nord and Ericsson (1985), Nord *et al.* (1985) and Ericsson *et al.* (1986), respectively. Magnetic order of some phosphate minerals vivianite (Gonser and Grant, 1967), ludlamite (Chandra and Hoy, 1967) and lithium orthophosphate $\text{LiFe}_{0.8}\text{Mn}_{0.2}\text{PO}_4$ (Schideler and Terry, 1969) at low temperature were examined.

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Triphylite-lithiophilite, sicklerite-ferrisicklerite and purpurite-heterosite with a similar structure are three important pegmatite solid solution series. The paragenetic relationships among primary and secondary phosphate minerals are very interesting and complex. Chemistry of phosphate minerals generally follows a fairly well-defined pattern:

The solid-solution series of triphylite-lithiophilite undergoes changes of oxidation states from Fe^{2+} to Fe^{3+} and from Mn^{2+} to Mn^{3+} , with simultaneous leaching out Li to maintain charge balance. Consequently, these cation alterations in the series cause the phase change to ferrisicklerite and purpurite.

Fe^{2+} or Fe^{3+} ions in one equivalent site in crystal structure of a paramagnetic mineral would produce one doublet in the Mössbauer spectrum. However, substitution of different cations into the site produces variations in the local next nearest neighbor (NNN) configuration and variable electric field gradients in Fe^{2+} or Fe^{3+} ions. Therefore, the multiple doublets with nearly equal isomer shifts but slightly different quadrupole splittings in the Mössbauer spectrum may be formed. This so-called NNN effect should be quite common in minerals. However, such effects have been identified only in the Mössbauer spectra of some minerals with less complex structures. Since Dowty and Lindsley (1973) first observed the NNN effect in the Mössbauer spectra of hedenbergite-ferrosilite solid solution, the effects have been identified in natural C2/c and P2/c omphacite (Aldridge *et al.* 1978), synthetic Ca-Na pyroxene solid solution (Dollase and Gustafson, 1982), spinel and chromite (Riedel and Karl, 1980; Bancroft *et al.* 1983; Li and Stevens, 1986; Li *et al.* 1988a; Chen *et al.* 1992) as well as wustite (McCammon and Price, 1985).

The Mössbauer spectra of these phosphate minerals at 298K consist of the multiple doublets with broad absorption peaks, of which doublets have nearly equal isomer shifts but slightly different quadrupole splittings. These multiple doublets may be contributed from Fe^{2+} or Fe^{3+} in the cation sites of the structure of these minerals. This suggests that NNN effects can be applied to explain the Mössbauer spectra of these three phosphate minerals. In this paper the Mössbauer effects of triphylite, ferrisicklerite and purpurite were investigated, and NNN effects were used to explain the Mössbauer spectra of the three phosphate minerals.

Experimental

The specimens from a granite pegmatite, Xinjiang province, China were used for this study. The chemical compositions of three samples were analyzed by Cameca SX 51 electron probe microanalyzer. Six representative small crystals for each sample were chosen to subject to electron microprobe measurements. Volatile components in these specimens were analyzed by wet chemical method. Table 1 presents the average compositions of three phosphate minerals.

TABLE 1. The chemical compositions of three phosphate minerals.

Sample	Na ₂ O	K ₂ O	CaO	MgO	FeO	MnO	Mn ₂ O ₃	P ₂ O ₅	SiO ₂	Al ₂ O ₃	H ₂ O	Volatile	Total
Triphylite	0.15	0.06	0.07	1.74	33.96	8.05		45.68	0.12	0.06		1.62	91.51
Ferrisicklerite	0.07			0.03	6.78	39.72		46.98					93.58
Purpurite	0.02	0.19	0.17	0.29	14.44		35.40	47.86			0.31		98.68

X-ray powder diffractions of these specimens showed that no impurities exist in these specimens. Triphylite Li(Fe,Mn)PO_4 and ferrisicklerite $\text{Li}_{1-x}\text{Mn}^{2+}_{1-x}\text{Fe}^{3+}_x\text{PO}_4$ certainly contain Li ions. As we had not enough samples for wet chemical method to determine Li contents in triphylite and ferrisicklerite, we suppose that the remaining components in these two samples are lithium oxide Li_2O . Here the chemical formulae can be written as following:

Triphylite: $(\text{Li}_{0.897}\text{Na}_{0.008}\text{K}_{0.002}\text{Ca}_{0.002}\text{Fe}^{2+}_{0.059})_{0.968}(\text{Mg}_{0.071}\text{Al}_{0.002}\text{Mn}^{2+}_{0.179}\text{Fe}^{2+}_{0.687})_{0.939}(\text{Si}_{0.003}\text{P}_{1.016})_{1.019}\text{O}_4$

Ferrisicklerite: $(\text{Li}_{0.654}\text{Na}_{0.003})_{0.657}(\text{Mn}^{2+}_{0.600}\text{Mn}^{3+}_{0.246}\text{Fe}^{2+}_{0.024}\text{Fe}^{3+}_{0.119})_{0.989}\text{PO}_4$

Purpurite: $(\text{Na}_{0.001}\text{K}_{0.006}\text{Ca}_{0.004}\text{Mg}_{0.011}\text{Mn}^{2+}_{0.230}\text{Mn}^{3+}_{0.435}\text{Fe}^{2+}_{0.018}\text{Fe}^{3+}_{0.279})_{0.984}\text{PO}_{3.813}(\text{OH})_{0.051}$

The ratios of Fe^{2+} to Fe^{3+} in ferrisicklerite and purpurite were obtained based on the Mössbauer analyses. After ratio $\text{Fe}^{3+}/\text{Fe}^{2+}+\text{Fe}^{3+}$ was determined by Mössbauer method, weight percentage of total oxides in ferrisicklerite is only increased by 0.96%(from 100% to 100.96%). This slight change can be considered within error range.

The ^{57}Fe Mössbauer spectra of three phosphate minerals were recorded in transmission geometry using a constant acceleration spectrometer. Gamma-ray source of $\sim 5\text{ mCi } ^{57}\text{Co}$ in palladium matrix was used. Doppler velocity was calibrated using a metal iron foil. The Mössbauer spectra were fitted to the pure Lorentzian lines using a computer program. The line widths and intensities of the component peak of each doublet were constrained to be equal.

Results

Figs. 1 (a), (b) and (c) show the Mössbauer spectra of triphylite, ferrisicklerite and purpurite at room temperature (298K), respectively. The spectrum of triphylite is composed of three Fe^{2+} doublets, and two of them are assigned to Fe^{2+} ions in the octahedral M2 site in the crystal structure of triphylite, and one of them to Fe^{2+} in the M1 octahedral site. The spectrum of ferrisicklerite consists of three doublets, and two of them are contributed from Fe^{3+} ions in the M2 octahedral site, and one of them from Fe^{2+} in the M2 octahedral site in the crystal structure of ferrisicklerite. The spectrum of purpurite is fitted to four doublets, and three of them are ascribed to Fe^{3+} in the octahedral M2 site in the crystal structure of purpurite, and one of them to Fe^{2+} in the M2 octahedral site. The Mössbauer parameters and assignments were given in Table 2.

Discussion

Triphylite

The crystal structure of triphylite was determined by Finger and Rapp (1970). It is close to that of olivine. Triphylite structure consists of $(\text{Li}, (\text{Mn}, \text{Fe}))\text{O}_6$ octahedra linked by common edges into zigzag chains which are linked by PO_4 tetrahedra. Half of the octahedral voids are occupied by M atoms (Li, Mn, Fe) and one-eighth of tetrahedral voids by P atoms. The metal atoms (Li, Mn, Fe) occupy two kinds of non-equivalent positions: half are located at the centers of symmetry, labeled as M1, and half on reflection planes, labeled as M2. Both M1 and M2 sites are analogous to those in the olivine structure. Finger and Rapp (1970) showed that Li and (Mn, Fe) occupied the M1 and M2 sites, respectively. The average bond distances for the M1 and M2 sites are 2.15 Å and 2.163 Å, respectively. Each M1 octahedron shares edges with two other M1 octahedra, two M2 octahedra and two P tetrahedra. Each M2 octahedron shares edges with two M1 octahedra and one P tetrahedron.

According to the chemical formula of triphylite, 0.897 Li and 0.012 (Na, K and Ca) ions are ordered in the octahedral M1 site and P ions occupy the tetrahedral site. The present Mössbauer study shows that 0.059 Fe^{2+} (8% of total iron) is in the M1 site. Since there is only a small amount of Na, K, Ca and Fe in the M1 site of the crystal structure of triphylite, the substitution of these cations at the M1 site can be neglected in the influence of local electric environment. In addition, P ions only occupy the tetrahedral site. This suggests that the octahedral M1 site and the tetrahedral site would not bring the variations in the local NNN configuration at Fe^{2+} in the M2 site.

FIG. 1 The Mössbauer spectra of triphylite (a), ferrisicklerite (b) and purpurite (c) at 298 K.

TABLE 2. The Mössbauer parameters of triphylite, ferrisicklerite and purpurite at 298K.

Sample	$\delta(\text{mm/s})$	$\Delta(\text{mm/s})$	$\Gamma(\text{mm/s})$	A(%)	Assignment	Doublet	χ^2
Triphylite	1.22(1)	2.98(1)	0.31(3)	72	$\text{Fe}^{2+}(\text{M2})$	A	1.27
	1.19(1)	2.76(5)	0.26(3)	20	$\text{Fe}^{2+}(\text{M2})$	B	
	1.20(2)	1.74(4)	0.30(3)	8	$\text{Fe}^{2+}(\text{M1})$	C	
Ferrisicklerite	0.46(1)	1.04(5)	0.38(1)	56	$\text{Fe}^{3+}(\text{M2})$	A	1.06
	0.47(1)	0.75(4)	0.26(3)	27	$\text{Fe}^{3+}(\text{M2})$	B	
	1.21(1)	2.92(2)	0.35(2)	17	$\text{Fe}^{2+}(\text{M2})$	C	
Purpurite	0.42(1)	1.69(1)	0.27(4)	58	$\text{Fe}^{3+}(\text{M2})$	A	1.26
	0.40(1)	0.96(13)	0.40(10)	21	$\text{Fe}^{3+}(\text{M2})$	B	
	0.38(1)	0.56(7)	0.29(5)	15	$\text{Fe}^{3+}(\text{M2})$	C	
	1.20(3)	2.92(5)	0.27(4)	6	$\text{Fe}^{2+}(\text{M2})$	D	

* $\delta(\text{mm/s})$ are relative to α -iron.

In the triphylite structure each M2 octahedron shares corners with four M2 octahedra. Since the M2 site is mainly occupied by Fe^{2+} and Mn^{2+} ions, the substitution of Fe^{2+} for Mn^{2+} in the M2 site may cause a variety of electric field gradients in the M2 site. Therefore, two doublets with $\delta = 1.22 \text{ mm/s}$, $\Delta = 2.98 \text{ mm/s}$ and $\delta = 1.19 \text{ mm/s}$, $\Delta = 2.76 \text{ mm/s}$ are contributed from Fe^{2+} in the M2 site, indicating that the NNN effect was recognized in the Mössbauer spectra of triphylite. Very small amounts of Mg and Al occupy the M2 site in the crystal structure of triphylite, then the local NNN combinations between those ions and $\text{Fe}^{2+}(\text{Mn}^{2+})$ in the M2 site can be neglected.

If the site occupancy is truly random, the probability $P(n)$ of finding the number (n) of Fe ions and the number ($N-n$) of Mn in the four M2 sites shared corners with the M2 site is given by the binomial distribution:

$$P(n) = (N!/n!(N-n)!) (1-c)^{4-n} c^n \quad (1)$$

where c and $(1-c)$ are the occupancies of Fe^{2+} and Mn^{2+} in the M2 site, respectively, N is the number of next nearest neighbor atoms. For triphylite, $N=4$.

Table 3 presents the possible cation combinations ($n=0,1,2,3$ and 4), Mössbauer absorption ratios and assignment of Fe^{2+} doublets to the corresponding cation combinations. The quadrupole splittings of the third doublet in the Mössbauer spectrum of triphylite is 1.74 mm/s . This value is much smaller than those of other two doublets, suggesting that this doublet may be contributed from Fe^{2+} in the M1 site. Nord and Ericsson (1986) and Kostiner (1972) investigated the Mössbauer effects of farringtonite and triploidite, respectively. The quadrupole splitting of Fe^{2+} in the octahedral M(2) site of farringtonite was reported to be 1.78 mm/s , and the corresponding parameter of Fe^{2+} in the octahedral M(2,3,5,7) site of triploidite is 1.77 mm/s . The value of the quadrupole splitting of Fe^{2+} in the M1 site of triphylite is very close to that obtained by Nord and Ericsson (1986) and Kostiner (1972). From the tri-

phylite formula it can be seen that there is not enough amounts of Li, Na, K and Ca ions in the M1 site. So small amounts of Fe^{2+} may occupy remaining the M1 site. This is coincident with the Mössbauer analyses of triphylite.

Ferrisicklerite

Ferrisicklerite is an intermediate product from the oxidation of triphylite. In ferrisicklerite ferrous ions are totally or partially oxidized to ferric ones. Ferrisicklerite has the same structure of triphylite, in which Li and (Fe,Mn) occupy the M1 and the M2 sites, respectively. According to the formula of ferrisicklerite, 65.7% of the M1 site are occupied by Li (65.4%) and Na (0.3%) ions, and remaining 34.3% of the M1 site are empty. It is the same as triphylite that each M2 octahedron in ferrisicklerite structure shares edges with two M1 octahedra and corners with four M2 octahedra. The bond distances between the ions in the edge shared M2 and M1 cations are shorter than that in the corner shared M2 and M1 octahedra, the local environment in the M2 site is mainly controlled by the different NNN arrangements between Li ions (65.4%) and voids (34.3%) in the M1 site. Here the influence from the ions in the M2 site may be neglected compared with those in the M1 site.

If the site occupancy is truly random similar to triphylite, the probability of finding (n) Li and (2-n) voids in the two M1 site is given by the equation (1). In this case $N=2$, c is the occupancy of Li in the M1 site, (1-c) is the possibility of the voids in the M1 site. The assignment of Fe^{3+} doublets to the different cation combinations is given in Table 3. The doublets with $\delta = 0.46$ mm/s, $\Delta = 1.04$ mm/s and $\delta = 0.47$ mm/s, $\Delta = 0.75$ mm/s at 298 K are ascribed to Fe^{3+} in the M2 site in the crystal structure of ferrisicklerite, while the doublet with $\delta = 1.21$ mm/s and $\Delta = 2.92$ mm/s is assigned to Fe^{2+} ions in the M2 site.

Purpurite

Purpurite is formed by oxidation of triphylite and ferrisicklerite with simultaneous

TABLE 3. The assignment of Fe doublets to the cation combination

Triphylite	a	4Mn^{2+}	$1\text{Fe}^{2+}3\text{Mn}^{2+}$	$2\text{Fe}^{2+}2\text{Mn}^{2+}$	$3\text{Fe}^{2+}1\text{Mn}^{2+}$	4Fe^{2+}
	b	0	0.02	0.15	0.41	0.42
	c	Doublet A	(0.22)		Doublet B (0.78)	
ferrisicklerite	a	2Li^{1+}			$1\text{Li}^{1+}1\text{V}$	2V
	b	0.43			0.45	0.12
	c	Doublet B	(0.33)		Doublet A (0.67)	
Purpurite	a	$4\text{Mn}^{2+}(\text{Fe}^{2+})$	$3\text{Mn}^{2+}(\text{Fe}^{2+})$ $1\text{Mn}^{3+}(\text{Fe}^{3+})$	$2\text{Mn}^{2+}(\text{Fe}^{2+})$ $2\text{Mn}^{3+}(\text{Fe}^{3+})$	$1\text{Mn}^{2+}(\text{Fe}^{2+})$ $3\text{Mn}^{3+}(\text{Fe}^{3+})$	$4\text{Mn}^{3+}(\text{Fe}^{3+})$
	b	0.01	0.05	0.22	0.42	0.30
	c	Doublet C	(0.16)		Doublet B (0.22)	Doublet A (0.62)

(a) The different combinations between two kinds of ions, V represents the void in the M1 site;

(b) The probabilities calculated based on equation (1);

(c) The doublet and ratio of the the Mössbauer absorption.

leaching out Li ions. The crystal structure of purpurite-heterosite was determined by Eventoff *et al.* (1972). The basic features of purpurite structure is derived from the parent phase triphylite through leaching out Li ions from the M1 site and oxidation of Fe^{2+} and Mn^{2+} to Fe^{3+} and Mn^{3+} in the M2 site. Since the M1 site is not occupied by any atoms in the purpurite structure, this simplifies the local environment in the M2 site. Same as in triphylite, each M2 octahedron shares corners with four M2 octahedra. In the purpurite structure the M2 site is mainly occupied by Fe^{2+} , Fe^{3+} , Mn^{2+} and Mn^{3+} .

Since Fe^{3+} and Mn^{3+} have the same effective ionic radii (0.645 Å) and the same valence, both ions can make the same contribution to the electric field gradient in the M2 site. In addition, there is only a small amount of Fe^{2+} in purpurite. If the difference between the effective ionic radii of Fe^{2+} ($r=0.78$ Å) and Mn^{2+} ($r=0.83$ Å) is neglected, the different combinations between $\text{Mn}^{2+}(\text{Fe}^{2+})$ and $\text{Mn}^{3+}(\text{Fe}^{3+})$ would cause the different local environment in the M2 site. Similar to the triphylite, the NNN effect is predicted in the Mössbauer spectra of purpurite. Therefore, the doublets with $\delta = 0.42$ mm/s and $\Delta = 1.69$ mm/s, $\delta = 0.40$ mm/s and $\Delta = 0.96$ mm/s and $\delta = 0.38$ mm/s and $\Delta = 0.56$ mm/s in the Mössbauer spectrum of purpurite at 298 K are assigned to Fe^{3+} in the M2 site. According to the Mössbauer parameters the doublet with $\delta = 1.20$ mm/s and $\Delta = 2.92$ mm/s is ascribed to Fe^{2+} in the M2 site. The calculation of probability $P(n)$ was carried out by using equation (1), and the assignments of the Fe^{3+} doublets to the different cation combinations are presented in Table 3.

Summary

The crystal structures of primary and secondary phosphate minerals have similar features to that of olivine during these alteration processes except no atoms in the M1 site in the crystal structure of purpurite-heterosite. Octahedral M1 site is mainly occupied by Li ions in the crystal structures of triphylite-lithiophilite, while the M1 site in the crystal structure of purpurite-heterosite is empty. These simplify the local environment in the M2 site. Furthermore, from the chemical formulae of triphylite and purpurite studied here, the M2 site is mainly occupied by Mn and Fe ions and only very small amounts of Al, Mg and other ions are distributed over the M2 site.

The different combinations of Fe and Mn ions in the M2 site in triphylite and purpurite would produce a variety of electric field gradients in the M2 site. Therefore, the NNN effects were identified in the Mössbauer spectra of triphylite and purpurite. In the case of ferrisicklerite, 0.654 Li and 0.03 Na occupy the M1 site, and the remaining M1 site is vacant. The different NNN arrangements between Li and the voids in the M1 site mainly control the local environment in the M2 site. The NNN effect was also recognized in the Mössbauer spectrum of ferrisicklerite as the same in triphylite and purpurite.

If the NNN effects in three phosphate minerals were not considered, values are larger about 0.3-0.5 than the values listed in Table 2. This further shows that the NNN effects exist in the Mössbauer spectra of three phosphate minerals.

It can be seen that there are some differences between the probability calculations and the Mössbauer analyses for these phosphate minerals (Table 3). This may arise from the complexities in chemical compositions of these phosphate minerals or deviation from truly random distribution of ions in the M1 or M2 site.

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